ESRF	**Experiment title:** Structure evolution studies of sol-gel prepared PZT thin films	**Experiment number**: ME-69
Beamline: BM-29	**Date of experiment**: from: 14/02/00 to: 16/02/00	**Date of report**: 30/08/00
Shifts: 6	**Local contact(s)**: Michael BOROWSKI	*Received at ESRF:*

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1. Task

The challenge of this experiment is to measure EXAFS spectra (Pb and Zr edges, with the Pb edge receiving the greatest priority) of 200 nm thick PZT layers deposited on a 100 nm Pt electrode layer (Figure 1). Due to the small thickness of the PZT layers, measurements in absorption mode can be excluded beforehand. As will be shown, the measurement in fluorescence mode is complicated by the vicinity of Pt L peaks close to the Pb L peaks of interest. During the available measurement time at ESRF, we have investigated different approaches to address the interference of the underlying Pt layer with the layer of interest.

2. Experimental

In the first approach, we placed the sample (thin PZT film deposited on monocrystalline silicon and platinum) in the cryostat at a temperature of 50K. The fluorescence detector was positioned close to the sample and perpendicularly to the incoming beam. The results obtained in this working condition were not satisfactory. While EXAFS oscillations at the Pb L edge could be seen, the noise level was clearly too high. This was attributed to the presence, in the fluorescence spectrum, of intense Pt L peaks only 1-2 eV distant from the Pb peak of interest as shown in Fig.2a. Besides, a diffraction peak from the silicon substrate was observed in the absorption spectrum.

By tilting the sample in the cryostat with respect to the beam, the grazing incidence condition could be approached, and at the same time the diffraction peak was eliminated. As expected, we observed a decrease in the Pt peaks intensity by 1/3, but the overall intensity of the Pb L peaks remained rather low. As a result, the noise in the absorption spectrum was still too high to allow accurate recording of the absorption edge fine structure.

The gains obtained by tilting the sample convinced us that going to true grazing angle incidence would considerably improve the results. Therefore we placed a larger sample (1.5x3 cm) parallel to the beam on a

moveable sample holder which was then tilted by 0.55 degrees. The schematic set up is shown in Figure 3. We calculated that the grazing angle had to be between 0.2 and 0.8 degrees in order for the beam to illuminate the entire sample. We positioned the fluorescence detector in front of the sample holder, at a distance of few centimeter from the sample, inclined by ~13 degrees and perpendicular to the beam. To maximize the signal we choose an opening of the horizontal slits of 6 mm.
The effect of using the grazing incidence condition on the fluorescence spectrum was rather striking: the intensity of the Pt peaks was considerably reduced, while the Pb peaks were greatly enhanced. However the EXAFS oscillations were reduced in amplitude and the noise was still high. By going to an angle of 0.33 degrees, close to the true grazing incidence condition, the Pb L peak was further enhanced but at the same time the intensity of the EXAFS oscillations was damped. This damping was attributed to the saturation of the detector (high value of dead time, due to high beam intensity employed, giving rise to high noise level). By bringing down the beam intensity, through a reduction of the horizontal slit width to 0.6 mm, the EXAFS oscillations could again be observed, but the noise was not reduced. Finally, by positioning the detector 7 cm away from the sample to reduce the signal and setting the horizontal slits opening to 2 mm, a reasonable signal to noise ratio could be obtained. As a result, the quality of the EXAFS spectra could be considerably improved. Using the current approach, the remainder of the measurement time was used to record an average of 6 spectra for each of the 6 samples.

3. Data analysis

The data analysis was performed using the GNXAS[1] package by one of the authors (G.J.N.) during a one month stay at the University of Milano-Bicocca. A weighed average was taken of the spectra to take into account variations of the statistical noise. Figure 4 shows the averaged and background-substracted experimental data for sample 2 (annealed at 200°C, 2 min. followed by 400°C, 2 min). Phase shifts and backscattering amplitudes were calculated using PHAGEN employing Hedin-Lundqvist complex potentials within a muffin tin scheme. The experimental data was fitted to a 2-shell model for $PbTiO_3$ containing O as nearest neighbor and Ti as the second nearest neighbor using the fitting routine FITHEO. The model yielded bonding distances of 2.35 Å for a Pb-O and 3.3 Å for Pb-Ti. Figure 5 a and b show the dependence of the energy threshold E_o and the interatomic distances r(Pb-O) and r(Pb-Ti), obtained from the fit, on the upper bound of the fitting interval, E_{max}. For $13250 < E_{max} < 13450$, there is excellent agreement between the value of E_o obtained from the fit and the experimentally observed edge energy (13036 eV for all the data sets). This and the stability of r(Pb-O) in the same E_{max} interval is taken as evidence that the obtained value for r(Pb-O) is reliable. At the same time, due to the small energy range used for the fits, the correlation between the structural parameters σ and N in these fits is considerable, making an accurate determination of coordination numbers impossible. In conclusion, the noise on our data has to be considerably reduced in order to allow reliable extraction of first *and* second shell bonding distances and of coordination numbers.

4. Conclusions

The experiment turned out to be more complicated than expected. Two third of the assigned beam time was spent in finding the right condition to measure our samples. Only the Pb edge was measured, and the measurement time was not enough to allow the achievement of data with noise level below 2%. Nevertheless, we proved the feasibility of the EXAFS measurements on 200 nm thick PZT film in fluorescence mode by performing a physically meaningful fit to the EXAFS data and extract information about atomic geometry (Pb-O bonding distance). At the same time, the high noise on the data obtained using the present setup precludes the extraction of second shell parameters, which are however essential for the success of this experiment. Therefore, a continuation experiment is necessary in order to achieve our initial objective of obtaining detailed information on the bonding geometry of Pb in our samples.

[1] A. Filipponi, A. Di Cicco, T. A. Tyson, C. R. Natoli, Solid State Commun. **78** 265 (1991).

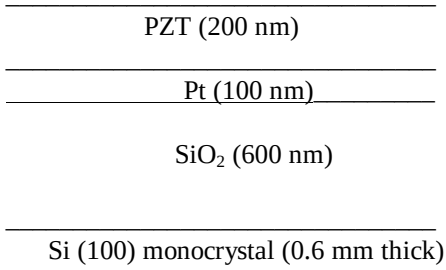


Fig. 1: Schematic cross section of the samples.

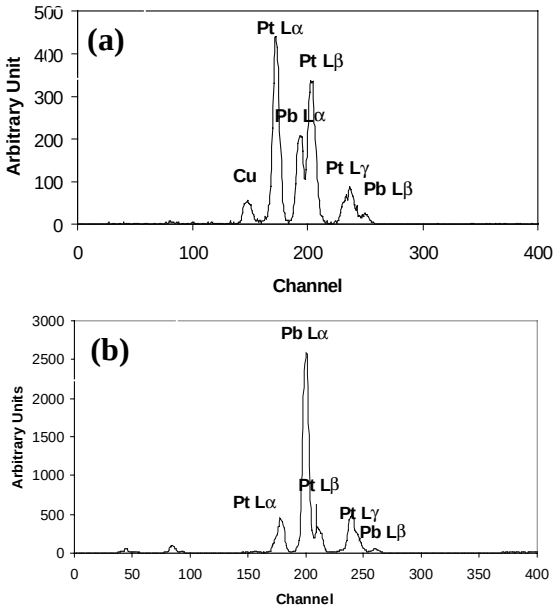


Fig. 2: Fluorescence spectrum for 200 nm PZT film on Pt. (a) using the initial setup in the cryostat; (b) the final measurements in grazing angle. The Pt L peak intensity is reduced and the intensity of the Pb L peak is enhanced.

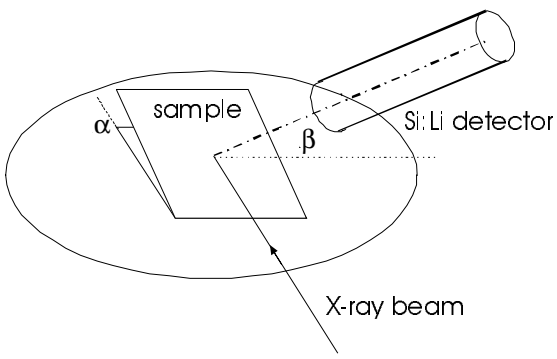


Fig.3: Schematic setup of the fluorescence measurement in grazing angle incidence.

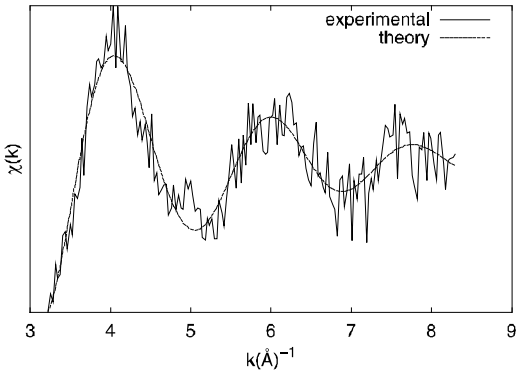
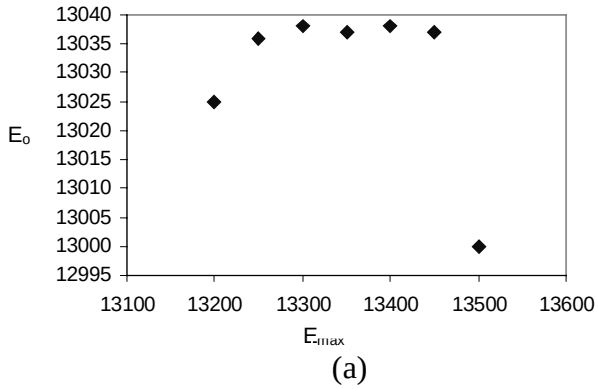


Fig. 4: Experimental Pb L-edge data, after background subtraction and conversion from energy to wave vector. The fit, using a two-shell $PbTiO_3$ model, is indicated.



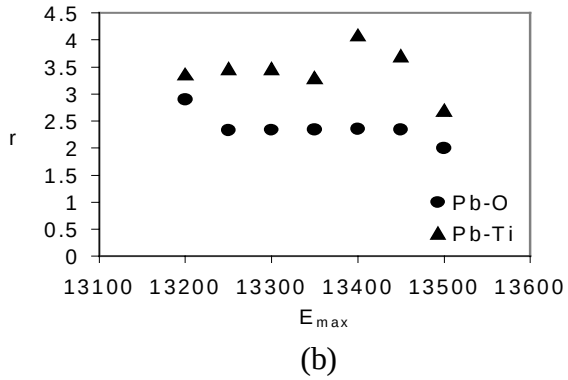


Fig. 5: (a) Dependence of the energy threshold E_o on the upper bound (E_{max}) of the interval used to perform the fits. (b) Dependence of the interatomic distances, r(Pb-O) and r(Pb-Ti), on E_{max}. For $13250 \leq E_{max} \leq 13450$, the fitting results are expected to be accurate because the fit is stable and E_o is close to the experimentally observed edge energy (E_{edge} = 13036).